

PATENT SPECIFICATION

NO DRAWINGS

1056.798

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Date of Application and filing Complete Specification: Oct. 11, 1963.

No. 40126/63.

Application made in Germany (No. D40075 IVd/39b) on Oct. 17, 1962.

Application made in Germany (No. D42275 IVd/39b) on Aug. 17, 1963.

Complete Specification Published: Jan. 25, 1967.

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Index at acceptance:—D1 P(AX, B5A, B5B, C2A9, C2A12AX, C2A12B4, C2A12B5, C2B3, C2C1, C2C6, C2C8, C2CX); C3 P(2C11, 2C13A, 2C13B, 2C13C, 2C14A, 2C14B, 2C16A, 2C16C, 2C20C, 2D1A, 2D8, 2FX, 2K7, 2K11, 2T2X, 11C11, 11C13A, 11C13C, 11C14A, 11C14B, 11C16A, 11C16C, 11C20C, 11D2A, 11D8, 11K2, 11K7); C3 Q(C11, C13A, C13B, C14A, C14B, C16A, C16C, C20C, D1A)

Int. Cl.:—D 06 m//C 08 c, d

COMPLETE SPECIFICATION

Improvements in the Bonding of Synthetic Textile Fibres to Rubber

We DUNLOP RUBBER COMPANY LIMITED a British Company of 1, Albany Street, London N.W.1. do hereby declare the inven-

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ERRATA

SPECIFICATION No. 1,056,798

Page 1, line 13, for "of" read "for"

Page 2, line 111, for "in" read "on"

Page 2, line 116, for "Emulsogen" read "Emulsogen L."

Page 3, line 12, for "sulphur" read "Sulphur"

THE PATENT OFFICE
27th February 1967

thetic fibre is a polyester and is treated by the process of the invention then the increase in the bond strength when compared with a polyester treated with a conventional adhesive based on a natural rubber latex mixed with a latex of a terpolymer of butadiene, styrene and vinyl pyridine can be as much as $2\frac{1}{2}$ times. The process of the invention is applicable when the synthetic fibre is in the form of a monofilament or in the form of cords to be used for instance to

The rubber latex that can be used can be any natural or synthetic latex or mixture of natural or synthetic rubber latices depending on the type of synthetic textile fibre to be treated. Typical examples of rubber latices are latices of copolymers of butadiene and vinyl compounds such as styrene, and terpolymers of butadiene, styrene and vinyl pyridine.

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COMPLETE SPECIFICATION

Improvements in the Bonding of Synthetic Textile Fibres to Rubber

We DUNLOP RUBBER COMPANY LIMITED a British Company of 1, Albany Street, London N.W.1. do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to providing synthetic textile fibres, to be used to reinforce rubber compositions, with a coating of an adhesive composition.

According to the present invention a process of providing a synthetic textile fibre with a coating of an adhesive composition comprises passing the fibre through an aqueous dispersion or emulsion of a masked isocyanate as hereinafter defined, an epoxy resin and a rubber latex.

The present invention provides a process whereby a synthetic textile fibre is provided with a coating of adhesive composition which when bonded to a rubber composition has a much higher bonding strength than when conventional adhesive mixtures are used for this purpose. For instance when the synthetic fibre is a polyester and is treated by the process of the invention then the increase in the bond strength when compared with a polyester treated with a conventional adhesive based on a natural rubber latex mixed with a latex of a terpolymer of butadiene, styrene and vinyl pyridine can be as much as $2\frac{1}{2}$ times. The process of the invention is applicable when the synthetic fibre is in the form of a monofilament or in the form of cords to be used for instance to

form the reinforcement plies for pneumatic tyres, though the process is particularly applicable when the synthetic fibre is a polyester an improvement in the bonding strength is obtained when the synthetic fibres is a polyamide, although not as great as the effect with a polyester fibre.

The masked isocyanate used is a compound that generates free isocyanate groups when heated and typical examples of such isocyanates are the aliphatic and aromatic isocyanates which have been reacted with a phenol to mask the isocyanate group. An example of a suitable masked isocyanate is tri-phenylmethane triisocyanate that has been reacted with phenol. Other examples of suitable masked isocyanates are phenol-blocked metaphenylene di-isocyanate and phenol-blocked methylene-bis-(4-phenylisocyanate).

The epoxy resin that is included in the adhesive composition can be any epoxy resin that can be formed into an aqueous emulsion or dispersion and typical epoxy resins are epoxidized polybutadiene or those based on reaction products of bisphenol A with epichlorhydrin.

The rubber latex that can be used can be any natural or synthetic latex or mixture of natural or synthetic rubber latices depending on the type of synthetic textile fibre to be treated. Typical examples of rubber latices are latices of copolymers of butadiene and vinyl compounds such as styrene, and terpolymers of butadiene, styrene and vinyl pyridine.

The proportions of the ingredients of the

aqueous dispersion or emulsion can vary over a wide range depending on the type of synthetic textile fibre treated and when the fibre is in the form of a monofilament then the proportion of the masked isocyanate to the rubber latex is much higher than when the synthetic textile fibre is in the form of a cord. However, it is preferable that the aqueous dispersion or emulsion should have a solids content of from 10 to 25% by weight in both cases. When the synthetic textile fibre is in the form of a monofilament then a convenient dispersion contains masked isocyanate and a rubber latex in a ratio of 8.5:1 on a dry basis and when the synthetic textile fibre is in the form of a cord the ratio can be 0.3:1. However, generally the ratio of the weight of the masked isocyanate to the weight of the latex can be from 10:1 to 0.2:1 on a dry basis. The proportion of the epoxy resin in the aqueous dispersion or emulsion can vary over wide limits and can be, for example, equal to the amount of the masked isocyanate or less than this amount when calculated on a dry basis. When the synthetic textile fibre is in the form of a cord then conveniently the amount of the epoxy resin present can be equal to the amount of the masked isocyanate and when the synthetic textile fibre is in the form of a monofilament then the amount of the epoxy resin can be less than the amount of the masked isocyanate. When the fibres are in the form of tyre cords then preferably the aqueous dispersion or emulsion also contains paraformaldehyde.

In carrying out the method of the invention the aqueous dispersion or emulsion can be prepared by mixing the masked isocyanate, epoxy resin and the latex and water if required in the presence of an emulsifying agent. Typical examples of emulsifying agents are soaps, alkyl aryl sulphonates, and polyether alcohols. Preferably a small proportion of an organic solvent is also incorporated in the aqueous dispersion or emulsion to assist dispersion and emulsification of the ingredients and the organic solvent is removed from the mixed ingredients prior to treatment of the synthetic textile fibre. Typical organic solvents which can be employed are methylene chloride and chloroform. A preferred way of forming the aqueous emulsion is to mix the masked isocyanate in the presence of water, an organic solvent and an emulsifying agent and to mix the emulsion so formed with a similar emulsion of the epoxy resin and with the rubber latex, and then to remove the organic solvent from the mixed emulsions.

The synthetic textile fibre is usually passed into the aqueous dispersion or emulsion at room temperature but a higher temperature can be used if desired and after treatment the coated fibre is allowed to dry. The drying process can comprise drying at room temperature followed by drying at a higher tempera-

ture. The coated fibre can be provided with a thin coating of a rubber composition and the rubberised fabric so obtained can be assembled into a number of articles in the usual manner and vulcanised. Typical articles that can be manufactured from the treated fibres are pneumatic tyres, driving belts, conveyor belts, hose, tarpaulins, containers for solids or liquids, and inflatable products such as life rafts.

The textile fibres can be in the form of a webless cord fabric to facilitate the production of rubber articles.

The process of the present invention provides a method of applying an adhesive composition to a textile fibre by a single step technique and is advantageous in that a considerable saving of labour and apparatus is effected when compared with multistage techniques.

The invention is illustrated in the following examples which all parts are given by weight.

EXAMPLE I

This example illustrates preparation and use of an adhesive composition for the treatment of polyethylene glycol terephthalate monofilaments.

An emulsion A was prepared from the following ingredients.

Parts by weight	
Phenol masked triphenylmethane triisocyanate	20
Chloroform	20
Water	60
Emulsifying Agent	1

A second emulsion B was prepared from the following ingredients,

Parts by weight	
Araldite D	20
Chloroform	20
Water	60
Emulsifying Agent	1

The name Araldite is a registered Trade Mark and Araldite D is an epoxy resin based in 4,4'-dihydroxyphenylpropane diglycidyl ether. The emulsions were each prepared by dissolving the masked isocyanate or the epoxy resin in the organic solvent and mixing with water. The emulsifying agent was obtained under the trade name Emulsogen.

100 gms of emulsion A were mixed with 20 gms of emulsion B and to the mixed emulsions were added 2 gms of a natural rubber latex having a 60% solids content and 3 gms. of a latex of a terpolymer of butadiene, styrene and vinyl pyridine containing 40% solids content and obtainable under the name Politone. The fibres to be treated were passed through the mixed emulsions and after passage were dried for 30 minutes at room temperature followed by 30 minutes at 130°C in a drying cabinet.

A rubber composition was prepared from the following ingredients.

	Parts by weight
5 Natural rubber	62.2
HMF Black	26.7
Zinc Oxide	3.7
Caoline	0.4
Stearic acid	0.5
Phenol R	0.8
10 Processing oil	3.6
Vulcazit CZ	0.4
sulphur	1.7

A block of the unvulcanized rubber composition was prepared with the coated monofilament passing through the block. The length of monofilament bonded within the block was 2 centimetres. The rubber compound was heated at a temperature of 160°C for 25 minutes under a pressure of 20 Kgms. per square centimetre. After vulcanization the block was stored for 24 hours at room temperature.

The force required to pull the monofilament from the vulcanized block was measured and a force of 15.5 Kgms. per test piece was required. In other words the force required to pull a monofilament which is bonded to rubber over a length of 2 centimetres from the rubber is 15.5 Kgms.

As a comparison the experiment was repeated employing as the adhesive composition a conventional adhesive based on a copolymer of butadiene and vinyl pyridine. The composition had the following formula-

	Parts by weight
Resorcinol	23.4
Formalin (30—33% solution)	56.0
40 NaOH (10% solution)	23.5
Butadiene Styrene Vinylpyridine terpolymer latex (40% solids)	290.0
NR-latex (20% solids)	193.0
45 Water	414.1

When the force to remove the filament from the vulcanized block of rubber was measured it was found that this was 0.2 Kgm per test piece.

It is clear from the above results that the process of the present invention is technically superior when compared with the use of the conventional adhesive composition.

If the adhesive composition used to treat the monofilament is based solely on the masked triisocyanate and the epoxy resin is omitted then the force required to remove the monofilament from the vulcanized slab of rubber is 6.5 Kgms per test piece.

EXAMPLE II

The experiment described in Example I was repeated but employing instead of Emulsion B an Emulsion C containing an epoxidized liquid polybutadiene. The epoxidized

polybutadiene was obtainable commercially under the name Oxiron 2000. When the emulsion containing the mixed isocyanate and emulsion C are mixed with amounts of the natural rubber latex and the latex of the copolymer of butadiene and vinyl pyridine as in Example I and applied to a monofilament then the force required to pull the monofilament from the block of vulcanized rubber is 15.5 Kgms per test piece.

EXAMPLE III

This example illustrates the treatment of polyester tyre cords.

60 parts by weight of emulsion A were mixed with 60 parts by weight of emulsion C and this mixture was added with careful stirring to a mixture of 100 parts of a latex of a terpolymer of butadiene, styrene and vinyl pyridine and 100 parts of water. Tyre cords formed from poly (ethylene glycol terephthalate) were passed through the composition and were then allowed to dry by drawing the cords through a tube carrying hot air at 130°C and then by storing in a drying cabinet for 60 minutes at a temperature of 130°C. The tyre cords were assembled as described in Example I with an unvulcanized rubber composition and vulcanized into blocks.

The force required to pull the tyre cords from the vulcanized block was 8 Kgms per centimetre length of cord bonded within the block.

A similar force was obtained when the adhesive composition includes in addition to the above-mentioned ingredients 30 parts of a natural rubber latex having a 60% solids content.

A force of 9.5 Kgms per centimetre was required when the adhesive composition contains in addition to the mixed emulsions A and C, 100 parts of a latex of a terpolymer of butadiene, styrene and vinyl pyridine and 10 parts of a natural rubber latex, 20 parts of a paraformaldehyde solution containing 40% paraformaldehyde and 100 parts of water.

WHAT WE CLAIM IS:—

1. A process for providing a synthetic textile fibre with a coating of an adhesive composition which comprises passing the fibre through an aqueous dispersion or emulsion of a masked isocyanate as hereinbefore defined, an epoxy resin and a rubber latex.

2. A process according to Claim 1 in which the fibre is in the form of a monofilament.

3. A process according to Claim 1 in which the fibre is in the form of a tyre cord.

4. A process according to Claim 3 in which a number of tyre cords assembled into the form of a webless cord fabric are treated.

5. A process according to any one of the preceding claims in which the solids content of the aqueous dispersion or emulsion is from 10 to 25% by weight.

6. A process according to Claim 5 in which the ratio of the weight of the isocyanate to the weight of the latex is from 10:1 to 0.2:1 on a dry basis.
- 5 7. A process according to Claim 2 in which in the aqueous dispersion or emulsion the ratio of the weight of the isocyanate to the weight of the latex is 8.5:1 on a dry basis.
- 10 8. A process according to Claim 3 or 4 in which in the aqueous dispersion or emulsion the ratio of the weight of the isocyanate to the weight of the latex is 0.3:1 on a dry basis.
- 15 9. A process according to any one of the preceding claims in which the amount of the epoxy resin is equal to or less than the amount by weight of the masked isocyanate when calculated on a dry basis.
- 20 10. A process according to any one of the preceding claims in which the masked isocyanate is triphenyl methane triisocyanate that has been reacted with phenol.
- 25 11. A process according to any one of the preceding claims in which the epoxy resin is epoxidized polybutadiene.
- 30 12. A process according to any one of Claims 1 to 10 in which the epoxy resin is based on a reaction product of bisphenol A and epichlorhydrin.
- 35 13. A process according to Claim 2 in which the rubber latex is a mixture of a natural rubber latex and a latex of a terpolymer of butadiene, styrene and vinyl pyridine.
14. A process according to Claim 3 or 4 in which the rubber latex is a latex of a terpolymer of butadiene, styrene and vinyl pyridine.
15. A process according to Claim 13 in which the monofilaments after passage through the adhesive composition are dried at room temperature followed by a higher temperature.
- 40 16. A process according to Claim 14 in which the tyre cords are dried after treatment with the adhesive composition by passing through heated air and/or by storing in a drying cabinet.
- 45 17. A process according to Claim 2 in which the monofilaments comprise a polyester.
- 50 18. A process according to Claim 3 or 4 in which the tyre cords comprise a polyester.
19. A process according to Claim 17 or 18 in which the polyester is poly (ethylene glycol terephthalate).
- 55 20. A process according to Claim 3 or 4 in which the adhesive composition contains para-formaldehyde.
21. A synthetic textile fibre having a coating of an adhesive composition when applied by a process according to Claim 1.
- 60 22. A pneumatic tyre having a textile reinforcement comprising polyester cords, said cords having adhesive composition applied to their surface by the process of Claim 1.
- 65 23. A process according to claim 1 for applying an adhesive composition to a synthetic textile fibre substantially as described in Example I or II.
- 70 24. A process according to claim 1 for applying an adhesive composition to a synthetic textile fibre substantially as described in Example III.
- C. H. BOWYER,
Agent for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1967.

Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

